
(12) UK Patent Application (19) GB (11) 2 027 921 A

(21) Application No 7926945 (54) **Coating compositions, their use and apparatus for curing them**

(22) Date of filing
25 Jul 1979

(23) Claims filed
25 Jul 1979

(30) Priority data

(31) 16235/78

(32) 25 Apr 1978

(33) United Kingdom (GB)

(43) Application published
27 Feb 1980

(51) INT CL³ G03C 1/68 //
G03B 21/16 C08F
2/50

(52) Domestic classification
G2C 1D3D 1G1 1GX
C6A
C3V BC
C3W 210 225 301
306C
C3Y B212 B215 B230
B240 B245 H660
G2J 41A1 41AX

(56) Documents cited
GB 1454191
GB 1408466
GB 1350260
GB 1198259
GB 1055198
GB 566795
GB 506309
GB 429173

(58) Field of search
G2C
G2X

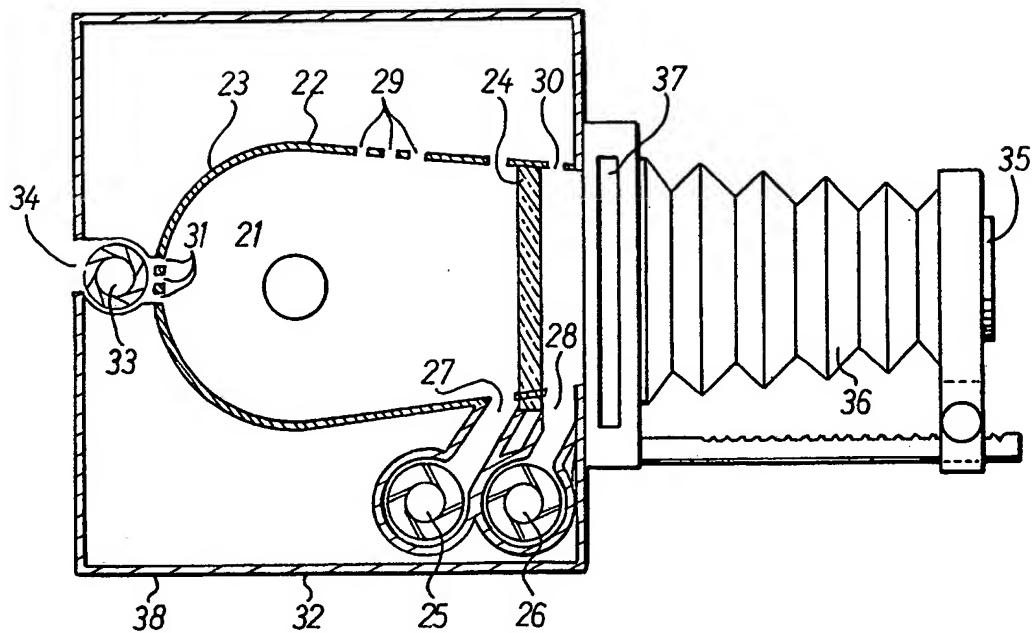
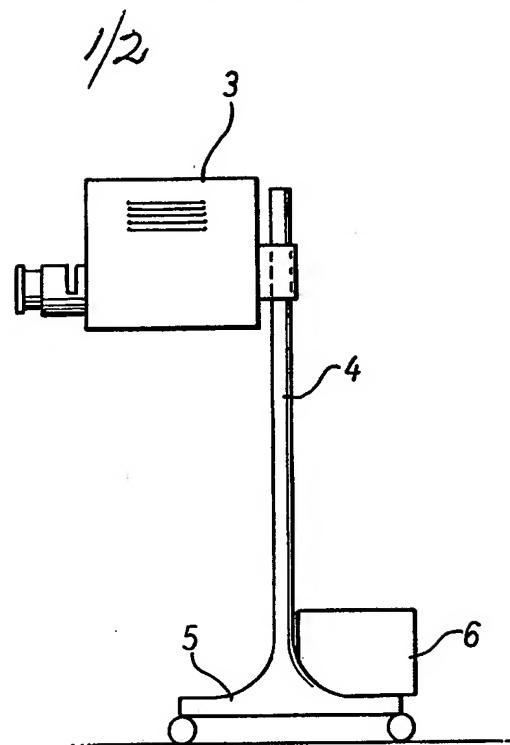
(71) Applicants
Kenneth Mapstone
33 Highfield Road
Walton
Liverpool
L9 1AS
Merseyside
James Richardson
1 Peel Walk
Maghull
Merseyside
L31 8DF

(72) Inventors
Kenneth Mapstone
James Richardson

(74) Agents
Messrs W P Thompson
& Co

GB 2 027 921 A

2027921



2027921

2/2.

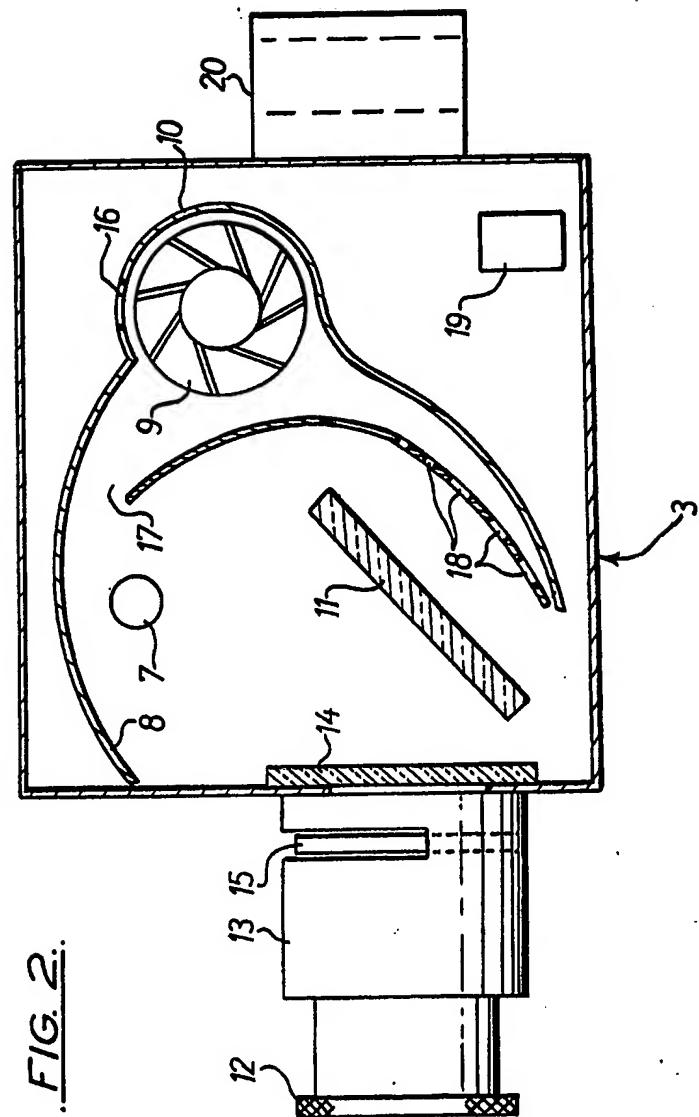


FIG. 2.

SPECIFICATION

Coating compositions, their use and apparatus for curing them

5 This invention relates to the graphic arts and to coating compositions, their use and apparatus for curing them. It is particularly concerned with signwriting and artwork especially when applied to transport vehicles. Such signwriting and artwork are normally applied to vehicles by hand painting, which is time consuming. There is a need to provide a quicker way of effecting such signwriting and artwork. 5

10 According to the present invention, there is provided an ultra-violet sensitive coating material which, when coated on a substrate, such as a vehicle body, may be cured by exposure to ultra-violet light. If the ultra-violet light is applied only to selected areas of the the coating, then only the selected areas of the coating are cured and the uncured areas of the coating may be removed, for example by washing, to leave a pattern of the coating on the substrate. 10

15 Signwriting and artwork may be applied to the substrate in this way and the areas to be irradiated may be selected by placing a stencil over the coating or projecting an image formed by the ultra-violet light onto the coating. The coating material may comprise a synthetic resin based paint or lacquer containing at least one radiation sensitiser which is able to sensitise the coating material to the ultra-violet light 15

20 whereby the coating material is cured or hardened on exposure to the ultra-violet light. The sensitiser normally functions as a photo initiator. The fact that the radiation is ultra-violet light and the fact that the coating material one which is curable by ultra-violet light allows the coating and exposing steps to be carried out in the presence of visible light. The only other principal step needed is the washing step to remove 20

25 uncured areas of the coating. The invention includes apparatus for forming an image in ultra-violet light. Such apparatus may take the form of a photographic enlarger or optical projector modified to project an ultra-violet image of a negative or transparency containing signwriting or artwork onto a substrate coated with material curable by ultra-violet light. The enlarger or projector may be modified by 25

30 providing an ultra-violet lamp as the light source and employing condenser and enlarging (or projecting) lenses made from a material which is capable of transmitting ultra-violet light, for example quartz. To protect the negative or transparency from the heat of the lamp, means may be provided for removing at least some of the heat before it reaches the negative. Thus a dichroic mirror may be positioned to transmit heat (infra-red radiation) from the lamp but reflect 30

35 ultra-violet light (and visible light) from the lamp through the lens system of the enlarger or projector. In more detail, the coating material may be photocurable composition for automobile 35

refinishing which comprises

(a) a polymerisable unsaturated monomer,

40 (b) a reactive polymer or oligomer,

(c) a pigmenting medium when desired,

(d) at least one photo initiator,

(e) if necessary or desirable, an activator for the photo initiator and

(f) thinner. 40

45 The monomer (a) must be a solvent for the polymer or oligomer (b) and must give a solution with acceptable solids-viscosity relationships that is to say the solution must be sprayable or spreadable. Ideally, it should have low volatility so as to minimise losses by evaporation when a film of the coating material is applied to a substrate. Finally, it should copolymerise readily with the unsaturated centres of the backbone, side chains or terminal groups of the polymer or 45

50 oligomer to give the required film properties. The most widely used monomers that satisfy these requirements are the vinyl aromatic compounds styrene and vinyl toluene (4-methyl styrene), the acrylic ester methyl methacrylate and some vinyl ethers for example trimethylolethane monoallyl ether $\text{CH}_3\text{C}(\text{CH}_2\text{CH}_2)\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$ and trimethylolpropane diallyl ether $\text{C}_2\text{H}_5\text{C}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2)_2\text{CH}_2\text{OH}$ but the monomers include other acrylic esters, for example methyl 50

55 acrylate, ethylene dimethacrylate, diethylene glycol diacrylate (SR-230), trimethylolpropane trimethacrylate (SR-350) and allyl acrylate; and vinyl esters, for example vinyl acetate. 55

The reactive polymer or oligomer (b) must have compatibility with the other components of the photocurable composition and have sufficient ethylenic unsaturation in the backbone, side chains or terminal groups to give the required degree of hardness by curing by free radical 60 polymerisation. Suitable ethylenically unsaturated reactive polymers include drying oils and semi-drying oils, reactive acrylic polymers, unsaturated polyesters (based on unsaturated diacid or diol), oxidising alkyd resins (containing drying or semi-drying oils), modified akyds (styrenated, epoxidised or methacrylated), or acrylate modified oligomers for example acrylated oils, acrylated, epoxies, acrylated polyesters and acrylated urethanes. 60

65 Examples of drying oils are linseed oil, tung oil, oiticica oil and perilla oil; examples of semi- 65

drying oils are dehydrated castor oil, tall oil, soyabean oil, and safflower oil. The reactive acrylic polymer group may be polymers or copolymers of acrylic acid, methacrylic acid, esters thereof (especially methyl or ethyl esters) and acrylonitrile, a suitable commercially available reactive acrylic polymer being Actomer X-80 (Union Carbide Corporation). 5

5 A suitable unsaturated polyester may be prepared by reacting a mixture of maleic anhydride and phthalic anhydride with propylene glycol. Examples of oxidising oil-based alkyd resins are a coconut oil alkyd prepred by the monoglyceride process from coconut oil, glycerine, and phthalic anhydride, a coconut oil alkyd prepared by the fatty acid process from coconut oil fatty acid, phthalic anhydride, glycerol and pentaerythritol, a linseed oil—pentaerythritol—phthalate 10 alkyd prepared by the fusion process, an isophthalic acid based alkyd prepared by the acidolysis process from soya bean oil, isophthalic acid and glycerine, and a water-soluble alkyd resin capable of drying by autoxidation and prepared from safflower oil, trimethylol propane, tetrahydrofurfuryl alcohol, trimellitic anhydride and phthalic anhydride. Such oil-based alkyds may have an oil length of for example 45 to 60% or more (percent by weight of oil in the alkyd) 15 and in general the oils used may be for example coconut, linseed, safflower, soya bean, tall, dehydrated castor or wood oil blends. An example of a modified alkyd resin is a methacrylated alkyd made by the copolymerization process from a soya bean oil/pentaerythritol/phthalic anhydride alkyd and methyl methacrylate. 15

The pigmenting medium (c) may comprise any pigments which will not interfere with the 20 ultra-violet curing process provided facilities are available for compounding and mixing. 20 Pigmented reactive polymers are commercially available. A preferred form of the invention uses a pigmented acrylic copolymer solution in a mixed ketone/ester solvent, for example a mixed acetone/ethyl acetate solvent.

The photoinitiators (d) absorb ultra-violet light and induce polymerisation of the polymerisable 25 components of the composition. It is believed that the polymerisation may be induced by a number of mechanisms, depending on the initiator system employed, as follows:— 25

1. Hydrogen abstraction by photo-excited molecules from the monomer or solvent to give radicals which initiate polymerisation.
2. energy transfer from excited initiator molecules to reactive double bonds in the composition components, 30
3. formation of a charge transfer excited state leading to ionic or radical induced polymerisation and/or
4. homolytic fragmentation of photoexcited molecules to yield radicals that directly initiate polymerisation.

35 Examples of suitable photoinitiators are benzoin and its derivatives, benzophenone and analogues, halogenated ketones, anthraquinone compounds, alkoxy ketones, sulphur compounds and some heterocyclic compounds. Certain synergistic mixtures have been found to be effective photoinitiators, particularly in pigmented systems. Thus an activator (e) may be mixed with the photoinitiator. Examples of such mixtures are benzophenone with an activator selected 40 from Michler's ketone, N-methyl diethanolamine, ethyl *p*-dimethylaminobenzoate, and dimethylaminobenzaldehyde; benzoin and Michler's ketone; 4,4'p dibenzoyl diphenyl sulphide and aniline; chloromethyl naphthalene and acetophenone; and 2-chlorothioxanthone with triethanolamine or 2, 3 bis-bromomethyl quinoxaline or ethyl *p*-dimethyl-aminobenzoate. 40

Examples of benzoin derivatives are ethers of benzoin and include the methyl, *i*propyl, *n*-butyl, *i*butyl and β -chloroethyl ethers of benzoin. Other derivatives of benzoin which may be used are α,α -dimethoxy γ -phenyl acetophenone and α,α -diethoxy γ -phenyl acetophenone. 45

Examples of the halogenated ketones and alkoxy ketones are 4-chloromethyl benzophenone; 4,4'-dichloromethyl benzophenone; γ,γ -dichloro (4-t-butyl) acetophenone; α,α -diethoxy acetophenone; α,α -dimethoxy acetophenone and 3,4-dimethoxy chalcone. 50

Examples of anthraquinone compounds are anthraquinone itself; 1,2-benzanthraquinone; 1-(β -bromoethyl) anthraquinone; 2-methyl anthraquinone and 2-t-butyl anthraquinone. 50

Examples of sulphur compounds for use as photoinitiators are 2-chlorothioxanthone, diphenyl disulphide and desylphenyl sulphide.

Heterocyclic compounds which may be used for example 2,3-dibromomethyl quinoxaline, 55 acridine and phenazine.

Other compounds which may be suitable as photoinitiators are the aromatic azido sensitizers which are often used in pre-sensitised printing plates and photo-resists. Under the action of photons e.g. when exposed to ultra-violet light, these azido compounds produce free radicals which can couple with another imine or react with some other molecule, such as the 60 unsaturation points in polyesters and oils. Examples of aromatic azido compounds are 4,4'-diazidostilbene-2,2' disulphonic acid; 4,4'-diazidostilbene α carboxylic acid; 4,4' diazido chalcone; 2, 6-di (4' azidobenzal)-cyclohexanone and 2, 6-di (4'azidobenzal)-4 methylcyclohexanone. 60

The invention includes a process for coating a substrate which comprises applying an ultra-violet sensitive coating material to the substrate and then exposing at least selected areas of it to 65 ultra-violet radiation to cure the material. The process may be used for coating substrates 65

included in the following forms of transport.

- (1) all types of aircraft.
- (2) all marine transport including boat, ships, hovercraft and submarines.
- (3) all forms of railway rolling stock, both coach finished and commercially finished.
- 5 (4) all types of motor vehicles, including cars, heavy and light commercial vehicles and motor cycles.

The process may also be applied to signboards of all descriptions and may be widely used in the advertising media. It can be applied to all substrates, whether flat, curved or undulating.

Other uses for the process involve using the fast curing compositions of the invention for fast 10 painting or coating of various objects. By irradiating them, coated objects may be cured and hence dried in seconds.

In addition to the photocurable compositions already described above, other coating materials such as cellulosic based paints and epoxy enamels may be sensitised to ultra-violet light and used in the process of the invention.

15 However, the photocurable acrylic compositions are preferred because they have the advantage that, as soon as selected areas of such acrylic compositions are irradiated with ultra-violet light, a chain reaction cross-linking takes place and the coating will cure itself once cross-linking has been initiated. Examples of suitable acrylic compositions described below:

20 **Composition A**

This is a total U.V. curing composition containing an oligomer, monomers and a photoinitiator.

The composition contains the following constituents in parts by weight:

25	Oligomer (a fully reacted aliphatic urethane acrylate)	—	66	25
	Phenoxy ethyl acrylate	—	20	
	Trimethylolpropane triacrylate	—	14	
	Irgacure 651 Photoinitiator (ex Ciba-Geigy)	—	4	
30	% NCO	—	Nil	30

The viscosity of the composition was determined on a Churchill Laray viscometer at 80°F:

35	Yield value	—	0 dynes/cm ²	
	Plastics viscosity	—	230 poise	35

The tack of the composition during curing was determined on a Churchill tackmeter at 300 r.p.m., 80°F.(27°C), 1 cm³ charge:

40	After Time			40
	0 minutes	—	32	
	½ minute	—	32	
	1 minute	—	32	
	2 minutes	—	30	
45	3 minutes	—	29	45
	4 minutes	—	28	
	5 minutes	—	27	

50 The composition cured at a 2 micron and 10 micron thickness when laid down on tin plate, polythene line board, and Thames white lined chip-board at speeds in excess of 800 ft/minute on a 2 lamped Primarc minicure unit. 50

The monomer in the composition has been reported to have a low skin irritancy.

Composition B

55 This is a U.V. curable base containing a fully reacted aliphatic urethane acrylate and a monomer. It can be converted to a U.V. curing composition by the addition of further monomer and photoinitiator.

The U.V. curable base has the following composition:

60	Oligomer (a fully reacted aliphatic urethane acrylate)	—	77%	60
	Phenoxy ethyl acrylate	—	23%	
	% NCO	—	Nil	

65 The viscosity of this composition was determined on a Churchill Laray viscometer at 65

80°F.(27°C):

Yield value — 0 dynes/cm²
 Plastics viscosity — 700 poise

5 The monomer in this composition has been reported to have low skin irritancy. 5

The U.V. curing composition contained the following constituents in parts by weight:

U.V. curable base	— 86	10
10 Trimethylolpropane triacrylate	— 14	
Irgacure 651 (ex Ciba-Geigy)	— 1	

15 The viscosity of this composition was determined on a Churchill Laray viscometer at 15 80°F.(27°C):

Yield Value	— 0 dynes/cm ²	
Plastics Viscosity	— 230 poise	20

20 The tack of the U.V. curing composition was determined on a Churchill tackmeter at 300 rpm, 80°F.(27°C.), 1 cm³ charge:

After time		
25 0 minutes	— 32	25
½ minute	— 32	
1 minute	— 32	
2 minutes	— 30	
3 minutes	— 29	
30 4 minutes	— 28	30
5 minutes	— 27	

The composition cured at a micron and 10 micron thickness when laid down on tin plate, polyethene lined board, and Thames white lined chipboard at speeds in excess of 800 ft/minute 35 on a 2 lamped Primarc minicure unit. 35

The invention includes the use of water-based acrylic compositions, such as Primal WL-81(Rhom and Haas), if a photoinitiator of the type described above is added to the composition to initiate curing on U.V. irradiation.

Primal WL-81, an aqueous emulsion of a thermoplastic acrylic resin is specifically designed 40 for formulation into both clear and pigmented lacquers for metal, plastic and wood substrates. It is high gloss, hard, water-based lacquer with good spray application. Primal WL-81 is supplied in water without co-solvent for maximum formulating latitude. With this vehicle, excellent water, salt spray, print and block resistance are obtained, without the flammability, odour, toxicity and other hazards of solvent-based industrial lacquers. Although designed for thermoplastic lacquers, 45 Primal WL-81 can be cross-linked with monomeric methoxy melamines to give harder, more resistant films. 45

Typical physical properties of Primal WL-81 are as follows:

Appearance	Milky white fluid	
50 Solids content, %	41.5	50
Volatile	Water	
Viscosity, cps	400	
pH	7.5	
Maximum fusion		
55 temperature, °C	57	55
Density	1.04 gms/cc	
Stability:		
Freeze thaw 5 cycles (-25°C/21°C)	Pass	
Mechanical, 4 min, Waring Blender	Pass	
60 Heat, 10 days at 60°C	Pass	60

The invention is illustrated in the following Examples; The Comparisons show that unless the compositions and the irradiating conditions are correct undesirable results are obtained.

65 Comparison 1 65

30g of Valacryl Blue acrylic based refinish paint (containing a previously pigmented acrylate polymer) were thinned with 30g of an acrylic thinner of ester and ketone formulation in which were dissolved 1g of benzophenone and 1g of N-methyl diethanolamine. The resulting sample was sprayed applied onto a test surface and the coating irradiated by means of a 6 watt medium pressure mercury vapour lamp through a step negative. No imaging was achieved after 30 minutes exposure. 5

Comparison 2

1.5g of benzophenone and 1.5g of N-methyl diethanolamine were dissolved in 10g of acrylic 10 thinners; then 15g of methyl methacrylate monomer, 15g of trimethylolpropane trimethacrylate and 30g of Valacryl Blue refinish paint were blended into the solution by agitation. A spray applied sample of the blend was irradiated for 20 minutes with a 6 watt medium pressure mercury vapour lamp but no imaging was achieved. 10

15 *Example 1* 15
A 4 mil wet thickness film of the blend of Comparison 2 was applied by doctor blade to a substrate and irradiated by means of a 400 watt medium pressure mercury vapour lamp for 15 minutes. The resultant image was developed by gentle swabbing with industrial methylated spirit to remove the unexposed, unhardened material. The final image was extremely hard, with 20 medium gloss and good colour saturation. 20

Comparison 3

1g of benzophenone and 1g of N-methyl diethanolamine were dissolved in a mixture of 10g of acrylic thinners, 10g of trimethylolpropane trimethacrylate and 10g of styrene monomer. 25 Subsequently 30g of Valacryl Blue refinish paint were added and the mixture stirred thoroughly. The mixture was sprayed onto a coated test piece to give a tacky coating which could not be hardened with radiation from a 6 watt mercury vapour lamp. 25

Example 2

30 Irradiation of the coating of Comparison 3 for 15 minutes by means of a 400 watt medium pressure mercury vapour lamp gave a hard semi-matt image which was developable with industrial methylated spirit. 30

Comparison 4

35 1g of ethyl p-dimethylaminobenzoate and 1g of benzophenone were dissolved in a mixture of 10g of acrylic thinners, 10g of trimethylolpropane trimethacrylate and 10g of styrene. The resultant solution was toned with 30g of Valacryl Blue refinish paint and sprayed onto a test panel. No cure was achieved with a 6 watt lamp. 35

40 *Example 3* 40
15 minutes exposure of the coating of Comparison 4 to a 400 watt mercury vapour lamp gave cured coatings developable with industrial methylated spirit. Some areas of the coating developed a matt appearance, possibly due to thickness variation.

45 *Example 4* 45
A mixture of 20g of methyl methacrylate, 12.5g of trimethylolpropane trimethacrylate and 12.5g of an acrylic polymer, Ebecryl 110 (Phenoxyethyl acrylate—Union Chemie Belge) was sensitised with 1.5g of benzophenone and 1.5g of ethyl p-dimethylaminobenzoate and then incorporated in 45g of a black acrylic refinish lacquer (Valacryl Black). The coating was applied 50 to test panels by doctor blade and irradiated for 15 minutes with a 400 watt mercury vapour lamp. Differential solubility of the exposed and unexposed areas was obtained but the final coating had patches of "alligator skin" texture on an otherwise matt black surface. 50

Comparison 5

55 A formulation was compounded consisting of 15g of Valacryl Black refinish lacquer, 1g of Benzophenone, 1g of ethyl p-dimethylaminobenzoate, 10g of methyl methacrylate and 10g of trimethylolpropane trimethacrylate. This material, when coated out, was exposed to light from the 400 watt ultra-violet source but after 15 minutes, no hardening of the coating was achieved. 55

60 *Comparison 6* 60
A sample of 5g of Valacryl Black acrylic lacquer was mixed with 15g of methyl methacrylate, 10g of Ebecryl 110 and 15g of trimethylolpropane trimethacrylate. The mix was sensitised with 1g of ethyl p-dimethylaminobenzoate and 1g of 2-Chlorothioxanthone. The coating cured after 65 10 minutes exposure to the 400 watt lamp but an objectionable texture was produced by virtue 65

of the undissolved 2-Chlorothioxanthone in the film and the colour was weak.

Example 5

The mixture in Comparison 6 was filtered to remove the undissolved 2-Chlorothioxanthone, 5 then 1g of benzophenone was added and the colour intensified by the addition of a further 10g of Valacryl Black Lacquer. After coating and exposing to an 1800 watt ultra-violet lamp a dense semi-matt black coating was achieved which was easily developable in industrial methylated spirit.

10 Example 6

To a mixture of 175g of an acrylated oil oligomer (Actomer X-70) and 70g of trimethylopropane triacrylate was added a photoinitiator blend in 10g of acetone and 22g of phenoxyethylacrylate. The photo initiator/activator system comprised 4g of benzil dimethylketal, 1g of isopropylthioxanthone, 3g of ethyl-*p*-dimethylaminobenzoate, and 0.5g of 9:10 phenanthrene quinone.

15 This material hardened in minutes in sunlight filtered through window glass.

Example 7

To 40g of the mixture prepared in Example 6 was added 3g of Chromophthal Red BR pigment dispersed in 5g of acetone, and the mixture vigorously dispersed by hand. A 2 mil wet 20 thickness film was applied by doctor blade to a substrate, and a U.V. image was projected on the film for approximately 8 minutes by means of the equipment described. A well defined 20 coloured image was obtained after swab development with industrial methylated spirit.

Example 8

25 As Example 7, but Chromophthal Blue A3R was used. The coating was rough in texture due to inadequate dispersion of the pigment.

Example 9

As Examples 7 and 8 but Chromophthal Yellow 3G was used. The coating was rough in 30 texture due to inadequate dispersion of the pigment.

Generally the curing the coating may be achieved with an ultra violet lamp having a wattage of 200 to 2000.

In the above Examples the coatings are developed, i.e. the unexposed parts are removed, by 35 washing with methylated spirit. It would be advantageous if instead of washing with an organic solvent, such as methylated spirit, the washing could be effected with water.

According to a further feature of the invention, the photocurable coating material contains a 40 solvent vehicle such as methanol which evaporates off from the coating material when it is applied, for example by spraying, to a substrate leaving a substantially dry coating. The coating material, which is sensitised with a photoinitiator and if desired is pigmented to any desired colour, is so composed that after curing by irradiation with ultra-violet light the unexposed parts may be removed by washing with water.

Thus at least one of the polymer-forming components of the coating material may be water-soluble. Such components include for example reactive monomers, co-monomers and copolymerisable polymers. Typical water-soluble monomers and co-monomers are acrylamide, 2-hydroxyethyl methacrylate, acrylic acid or its sodium salt, methacrylamide, N-isopropyl acrylamide, N-methyl acrylamide, N,N'-methylene bis acrylamide, and vinyl acetate. Suitable copolymerisable polymers are for example polyacrylamide, polyvinyl alcohol, water-soluble oxidising alkyds and unsaturated polyesters. Acrylic polymers are preferred.

50 In general the monomers, co-monomers and copolymerisable polymers should be soluble in both the solvent vehicle, for example an alcohol, and water. The copolymerised product obtained on irradiation should be water-insoluble. The photo initiator and, if present, the activator should be alcohol-soluble and, ideally, water-soluble.

The polymer solution, i.e. the polymer-forming components in the solvent vehicle, may be applied by spraying to a substrate. The solvent vehicle may be an alcohol-based solvent mixture 55 such as 74-OP (Industrial methylated spirits). After exposing selected areas of the coating to ultra-violet light, the unexposed, water-soluble non-image areas may be developed by spraying the coating with water. An example of this embodiment of the invention is given below.

Example 10

60 To a solution of 30g of acrylamide and 10g of 2-hydroxy ethyl methacrylate in 50g of the commercially available alcohol mixture 74-OP, 0.5g of benzophenone and 0.5g of N-methyl diethanolamine are added. The resultant solution was sprayed onto a test panel to form a coating which was irradiated in selected areas with an 1800 watt mercury vapour lamp to 65 polymerise the exposed areas of the coating. The unexposed areas were removed by spraying the coating with water.

Example 11

To 15g of linaqua, a polyether derivative of linseed oil, was added 7.5g of 2-hydroxy ethyl acrylate, 0.75g of benzophenone, 0.75g of N-methyl diethanolamine, and 3g of acetone. A 2 mil film hardened on exposure to light from a 1800 watt mercury lamp, and unexposed portions were developable by swabbing with water. 5

Example 12

To 15g of linaqua was added 5g of 2-hydroxyethyl acrylate, 2g of OTA 480 (a tri-functional acrylate oligomer), 0.75g of benzophenone, 0.75g of N-methyldiethanolamine, and 3g of acetone. A 2 mil wet film hardened in 5 minutes on exposure to a 1800 watt mercury lamp, and unexposed portions of the film were water developable. 10

Example 13

15 To 15g of linaqua was added 7.5g of 2-hydroxyethyl acrylate, 7.5g of acrylamide, 1g of benzophenone, 1g of N-methyldiethanolamine, and 6g of acetone. 15

The mixture gelled during mixing (ultrasonic) but the jelly was photocurable and could be reduced with thinners.

20 The invention will be still further described by way of example with reference to the accompanying schematic drawings in which: 20

Figure 1 is a side view of an ultra-violet projector assembly.

Figure 2 is a side view, on an enlarged scale and showing internal details of the projector unit shown in Fig. 1, and

Figure 3 is a modification of the projector unit shown in Fig. 2.

25 In Fig. 1, a projector unit 3 is slidable in a vertical direction on the upright 4 of a wheeled stand 5 which carries a control unit 6. If desired the projector unit may also be mounted so that it can be tilted up, down or sideways. 25

Mounted in the projector unit 3 shown in Fig. 2 are a quartz ultra-violet lamp 7 backed by a polished steel reflector 8, a turbo fan 9 in a chamber 10 and a dichroic mirror 11 inclined at 30 45° to the direction of the lamp and to the optical axis of a quartz lens 12 which is screw mounted for focussing in a lens barrel 13 carried by the projector unit 3. A quartz diffuser 14 is positioned between the mirror 11 and the lens 12. On the lens side of the diffuser, the lens barrel 13 is provided with a negative carrier 15. The fan chamber 10 is provided with an air inlet 16, an air outlet 17 directed towards the lamp and a plurality of air outlets 18 directed 35 towards the dichroic mirror. The projector unit 3 is also provided with a heat sensor control unit 19 for the fan and a mounting bracket 20 for mounting the unit 3 on the upright 4. 35

The ultra-violet lamp 7 is powered by the control unit 6 which may give an output of 300 volts. The lamp may be rated at 1800 watts and be tubular in form, for example 9" long by 1" diameter approximately.

40 The dichroic mirror 11 is coated to reflect ultra-violet and visible light i.e. light having wavelengths up to approximately 7000 Å. Infra-red light i.e. radiation having wavelengths longer than those of the visible spectrum will pass through the mirror, which is semi-transparent. The transmitted infra-red radiation comprises heat rays and the heat is dispersed by the fan 9 blowing air through the outlets 18. The reflected ultra-violet and visible light passes 45 through the lens 12. 45

The turbo fan 9 also blows air through the outlet 17 to cool the lamp and the fan is controlled by the heat sensor unit 19 which adjusts the speed of the fan to give the correct working temperature of the lamp for optimum operation.

45 The quartz diffuser 14 acts as an opalised screen and diffuses ultra-violet light to produce an even spread of ultra-violet and visible light over the area of the negative carrier 15. In place of or in addition to a quartz diffuser, a quartz condenser lens system may be used to give illumination of the negative carrier area. 50

The projection lens 12 is a compound lens made from high quality quartz. A suitable focal length for the lens is 150 mm with an aperture of 75 mm. As an alternative to screw focussing, 55 bellows focussing may be used. The effective focal length of the lens for ultra-violet light will be shorter than for the visible light and to facilitate focussing of ultra-violet images by the lens, the lens barrel 13 or the lens itself may be engraved with a focussing scale for the ultra-violet.

To facilitate ventilation of the projector unit 3, baffled vents (not shown) may be positioned at the sides of the casing of the unit for the discharge of warm air produced by the lamp 7.

60 In using the projector a negative is placed in the negative carrier and an image of the negative in ultra-violet light is focussed on a substrate which has been coated with a photocurable composition according to the invention. Curing of the exposed areas of the coating results and the unexposed areas are removed by washing to leave a positive image on the substrate. The negative may be a continuous tone or half tone negative. In the case of a half tone negative, the 65 image will be formed in dots. 65

The image may be formed in black and white or colour depending on the pigmenting of the photocurable composition. Multicolour images may be built up in layers using colour separation negatives, each of successive coatings of appropriate colour on the substrate being exposed in turn through a different negative.

5 The projector unit shown in Fig. 3 differs from that shown in Fig. 2 primarily in that the dichroic mirror is omitted. In Fig. 3, an ultra-violet lamp 21 is mounted in a chamber 22 at one end of which is a reflector 23, constructed of stainless steel, or preferably aluminium, burnished, or coated with a Lyman-alpha medium ($Mg F_2$). The reflection may be elliptical with the lamp at one of the foci, and the quartz diffuser or condenser 24 at the other. This is cooled by fan units 25 and 26 which are arranged to deliver a forced draught of air to opposite sides respectively of the diffuser through apertures 27 and 28 in the chamber 22. The chamber is further provided with vents 29 and 30 for discharge of air from the fan units and the reflector 23 has holes 31 located in it. The chamber 22 is mounted in a casing 32 and a further fan unit 33 is provided to suck hot air out of the chamber through the holes 31 and discharge it through an aperture 34 in the casing. A quartz lens 35, mounted in a twin track bellows focussing unit 36 carried by the casing 32, is positioned to focus the image of a negative positioned in the negative carrier 37 at the rear of the focussing unit, the image being formed in light from the ultra-violet lamp which has passed through the diffuser.

10 The rear section 38 of the casing 32 is hinged to facilitate removal of the lamp 21. The casing 32, like the unit 3 of Fig. 2, may be mounted on a stand as in Fig. 1 and the unit of Fig. 20 3 may be controlled by a remote control unit, which may be mounted on the stand. The unit of Fig. 3 is used generally in the same manner as that of Ig. 2. Various ultra-violet sources may be used according to the invention, for example:-

25 (a) *Arc Lamps* 25
 (1) Low pressure mercury vapour lamp,
 (2) Medium pressure mercury arcs,
 (3) High pressure mercury arc point source lamps,
 (4) Plasma arc radiation systems,

30 (b) *Lasers* 30
 Particularly Argon 111 (350-364nm)
 Krypton 111
 Pulsed Nitrogen (337nm)

35 Metal Vapour Lasers (325-441.6nm) 35
 (c) *Electrodeless Lamps*, or microwave excitation of mercury or rare gases.

(d) *Spectrally Enhanced Lamps*

40 Mercury vapour lamps (medium pressure) with various metallic elements, or metallic halides, introduced into the plasma discharge, for example iron iodide. 40

CLAIMS

1. Ultra-violet sensitive coating material comprising
- 45 2. Coating material as claimed in claim 1 wherein the monomer (a) is selected from vinyl aromatic compounds, acrylic esters, vinyl ethers, vinyl esters and mixtures thereof.
3. Coating material as claimed in claim 1 or 2, wherein the polymer or oligomer (b) is selected from drying oils, semi-drying oils, reactive acrylic polymers, unsaturated polyesters, oxidising alkyd resins, modified alkyds, acrylate modified oligomers and mixtures thereof.
- 50 4. Coating material as claimed in claim 1, 2 or 3 wherein the photoinitiator is used in admixture with an activator.
5. Coating material as claimed in claim 4, wherein the photoinitiator and the activator are alcohol-soluble and water-soluble.
6. Coating material as claimed in any one of claims 1 to 5, wherein a pigmenting medium is also present.
- 60 7. Coating material as claimed in claim 6 wherein the pigmenting medium is a pigmented acrylic copolymer solution in a mixed ketone/ester solvent.
8. Coating material as claimed in any one of claims 1 to 7 wherein a solvent vehicle is also present.
9. Coating material as claimed in any one of claims 1 to 7 wherein the monomer (a) is

65 water-soluble. 65

10. Coating material as claimed in any one of claims 1 to 7 wherein a solvent vehicle is also present and the monomer (a) is soluble in the solvent vehicle and water. 5

11. Coating material as claimed in any one of claims 1 to 10 cured by exposure to ultra-violet light. 5

5 12. A process for coating a substrate which comprises applying to the substrate a coating material as claimed in any one of claims 1 to 10 and then exposing at least selected areas of it to ultra-violet radiation to cure the exposed material. 10

13. A process as claimed in claim 12 wherein selected areas of the coated material are exposed to the ultra-violet light by placing a stencil over the material or by projecting an image formed by the ultra-violet light on to the material. 10

14. A process as claimed in claim 12 or 13 wherein unexposed areas of the coating material are removed by washing. 15

15. Apparatus for forming an image in ultra-violet light which comprises a photographic enlarger or optical projector capable of projecting an ultra-violet image of a negative or transparency. 15

16. Apparatus as claimed in claim 15 wherein an ultra-violet lamp is used as the light source and wherein condenser and enlarging (or projecting) lenses are used made of material which is capable of transmitting ultra-violet light. 20

17. Apparatus as claimed in claim 16 wherein a dichroic mirror is positioned to transmit heat from the lamp and to reflect ultra-violet light through the enlarger or projector. 20

18. Apparatus as claimed in claim 16 or 17, wherein the ultra-violet lamp has a voltage of 200 to 2000. 25

19. Coating material as claimed in claim 1 and substantially as hereinbefore described with reference to composition A or composition B. 25

25 20. A process as claimed in claim 12 (as dependent on claim 1) and substantially as hereinbefore described with reference to any one of Examples 1 to 13. 25

21. Apparatus as claimed in claim 15 and substantially as hereinbefore described with reference to and as illustrated in Figs. 1 and 2 or Fig. 3 of the accompanying drawings. 30

22. A process as claimed in claim 12 (as dependent on claim 1) and substantially as hereinbefore described with reference to the accompanying drawings. 30